Degradation of Silica and Sapphire Windows at Elevated Temperatures

N. S. Jacobson
NASA Glenn Research Center/HX5
Cleveland, OH 44135
nathan.s.jacobson@nasa.gov

High Temperature Electromagnetic Materials
National Academies
Washington, DC
March 2-3, 2023

Degradation of Oxides at High Temperatures

- In general, oxides are the most stable compounds
  - Silica and alumina are especially stable
  - Will not react with ambient oxygen or nitrogen

- But they do degrade at high temperatures
  - Fluxing (dissolution)
    - $SiO_2(s) + Na_2CO_3 \rightarrow Na_2SiO_3(liq) + CO_2(g)$
  - Direct vaporization
    - $SiO_2(s) \rightarrow SiO(g) + ½\ O_2(g)$

      $SiO_2(s) \rightarrow SiO_2(g)$
  - Enhanced vaporization
    - $SiO_2(s) + 2H_2O(g) \rightarrow Si(OH)_4(g)$

- Measurements/Methods
  - In vacuum
  - In atmosphere—look at higher ambient pressures; effect of enhanced vaporization
  - Computational—basic thermochemical data on vapor species using ab initio methods

- Modeling, predicting behavior

Vapor Phase may be Complex

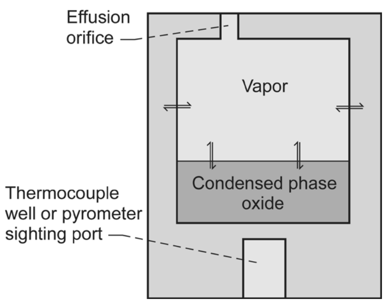
- SiO_2
  - In vacuum: $Si(g)$, $SiO(g)$, $Si_2O_2(g)$, $SiO_2(g)$, $O(g)$, $O_2(g)$
  - With water vapor: $SiO(OH)$, $SiO(OH)_2(g)$, $Si(OH)_4(g)$, $SiO(OH)_6(g)$, $Si_3O_2(OH)_8(g)$

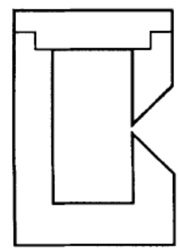
- Al_2O_3
  - In vacuum: $Al(g)$, $AlO(g)$, $Al_2O(g)$, $AlO_2(g)$, $Al_2O_2(g)$, $Al_2O_3(g)$
  - With water vapor: $AlO(OH)(g)$, $AlOH(g)$, $Al(OH)_2(g)$, $Al(OH)_3(g)$

- Accurate thermodynamic data for these species allows
  - Calculation of maximum vapor fluxes (material loss rate)
  - Models of applications, where diffusion is limiting. Thermodynamic data is an input to equations.

Equilibrium vs Langmuir Vaporization into a Vacuum

- Knudsen Cell

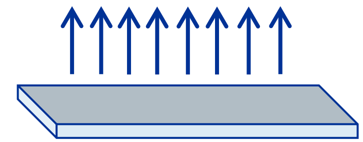




  – Obtain near equilibrium between condensed phase/vapor
  – First developed by Knudsen (Denmark), 1909: Measure Hg vapor pressures
  – Vapor effusing from orifice leads to a weight loss rate which relates to pressure; vapor can also be analyzed with spectrometer

$$J\,(\max) = \frac{P_{eq}}{\sqrt{2\pi MRT}}$$

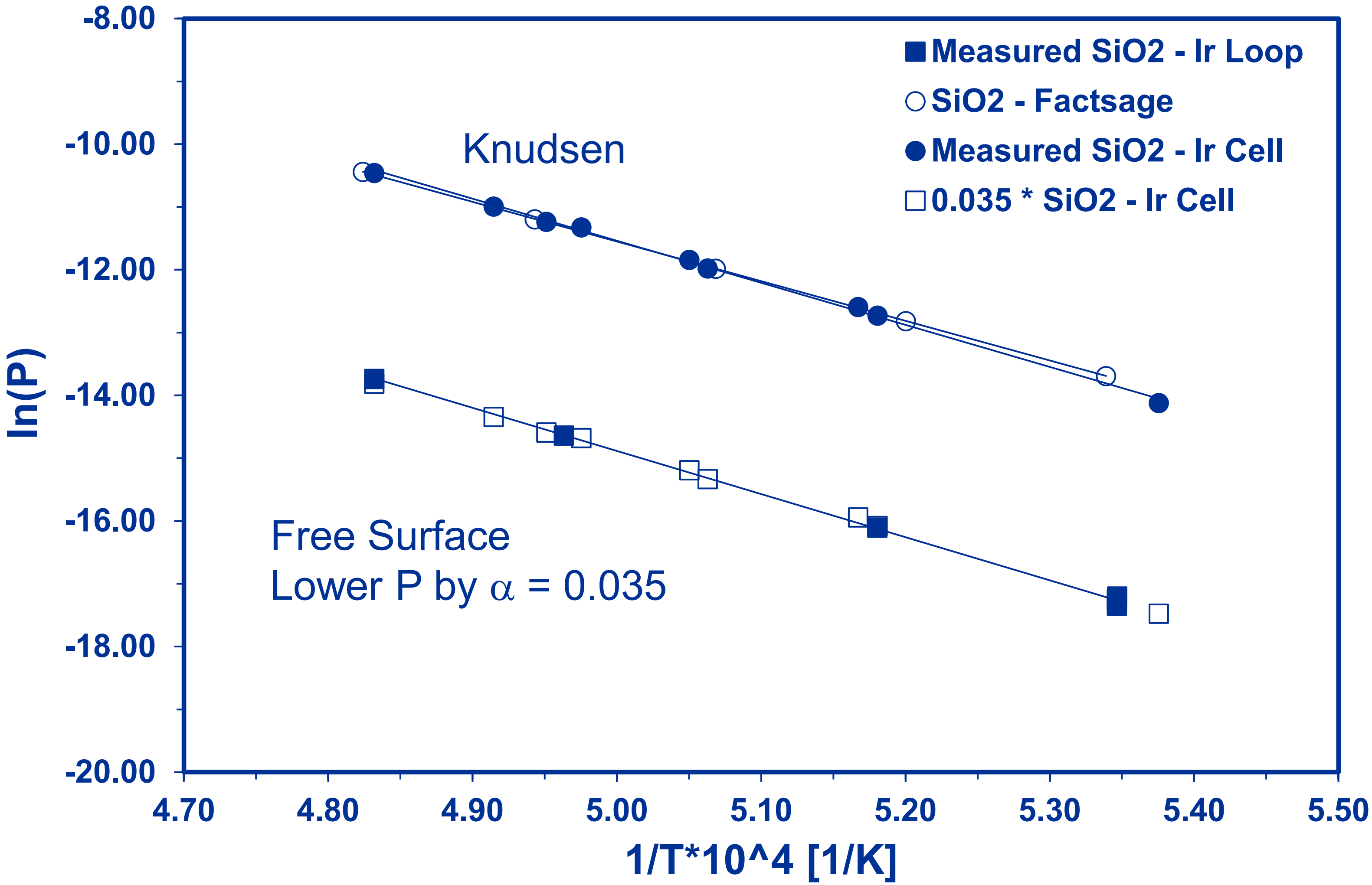
- Free Surface or Langmuir vaporization



  – Measure vaporization from flat faces with balance or mass spectrometer
  – Closer to application
  – Often has a kinetic step, accounted for by vaporization coefficient, α

$$J = \frac{\alpha P_{eq}}{\sqrt{2\pi MRT}}$$

Measured SiO_2 Knudsen and Free Surface Vaporization Coefficient = 0.035



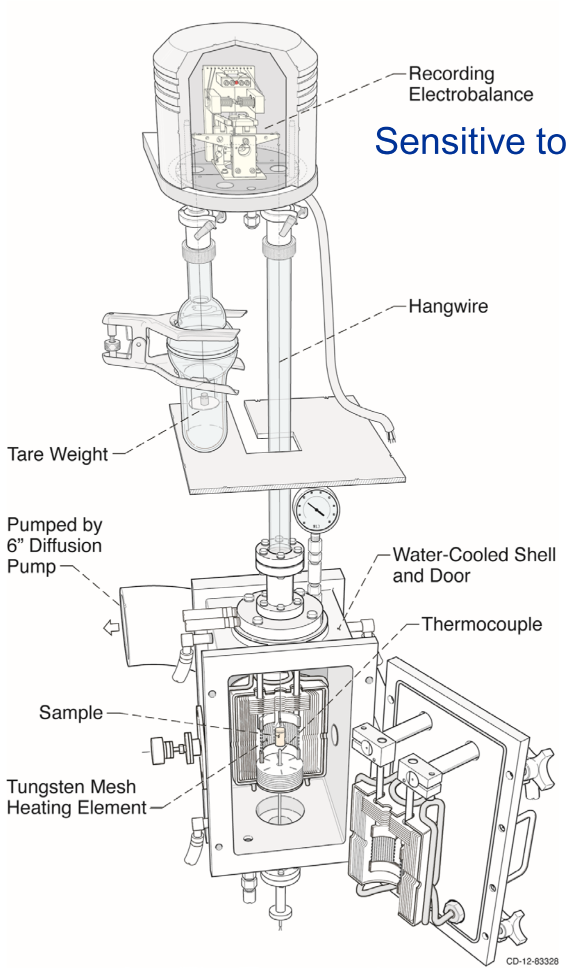
Kowalski et al., 2022

Experimental Methods

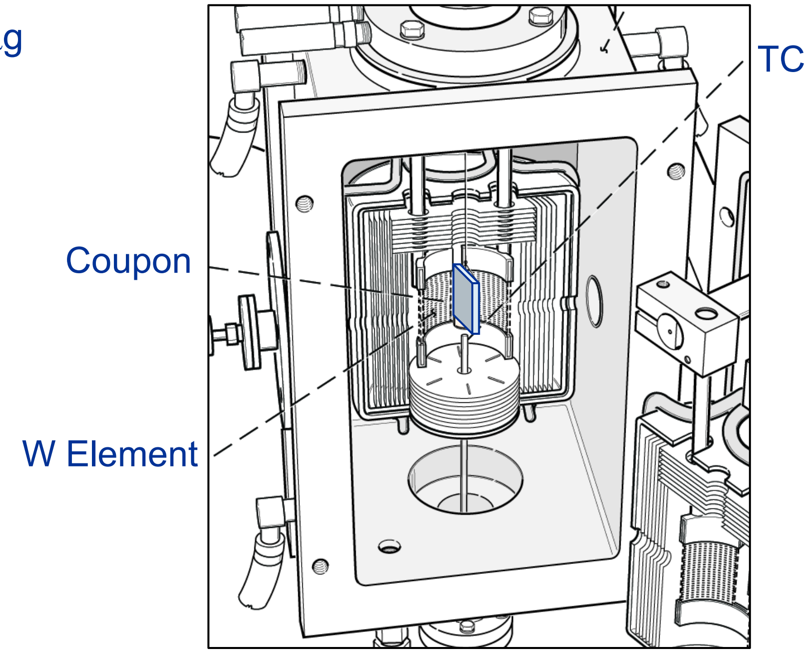
- Vaporization/degradation in a vacuum
  - Equilibrium/Knudsen or Free Surface/Langmuir
    - Vacuum thermogravimetric methods
      - Simple weight loss
    - High temperature mass spectrometry
      - Identify species and determine their partial pressures

- Vaporization/degradation into atmosphere
  - Reactive or non-reactive atmosphere
    - Flowing gas thermogravimetric methods
      - Simple weight loss
    - Transpiration
      - Get an accurate vapor pressure to determine thermodynamic data
    - High pressure sampling mass spectrometry
      - Identify species

Vacuum Microbalance—Direct measure flux from a Knudsen Cell (Equilibrium) or Coupon (Free Surface)

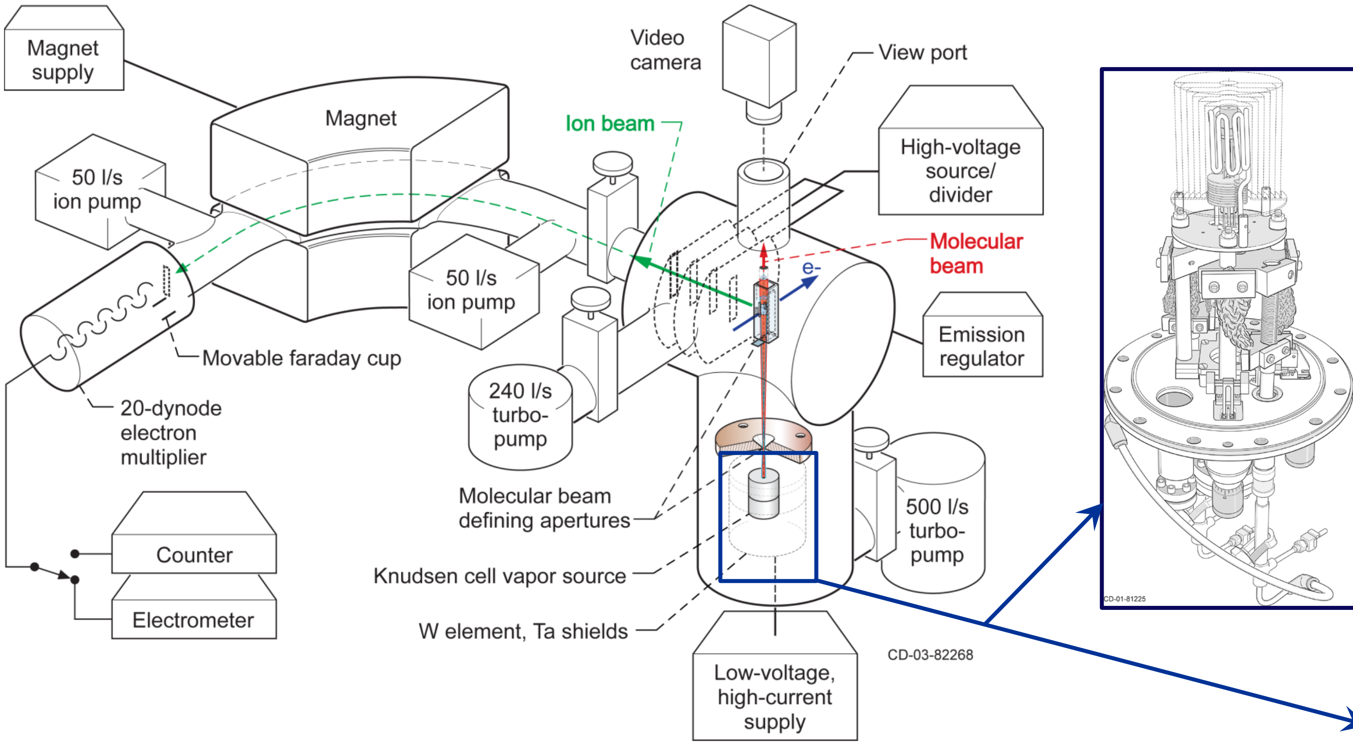


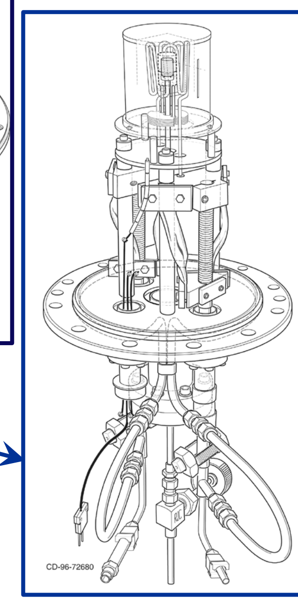
Sensitive to μg



- Measure flux (mg/cm^2-hr)
- $J = \frac{\alpha P_{eq}}{\sqrt{2\pi MRT}}$

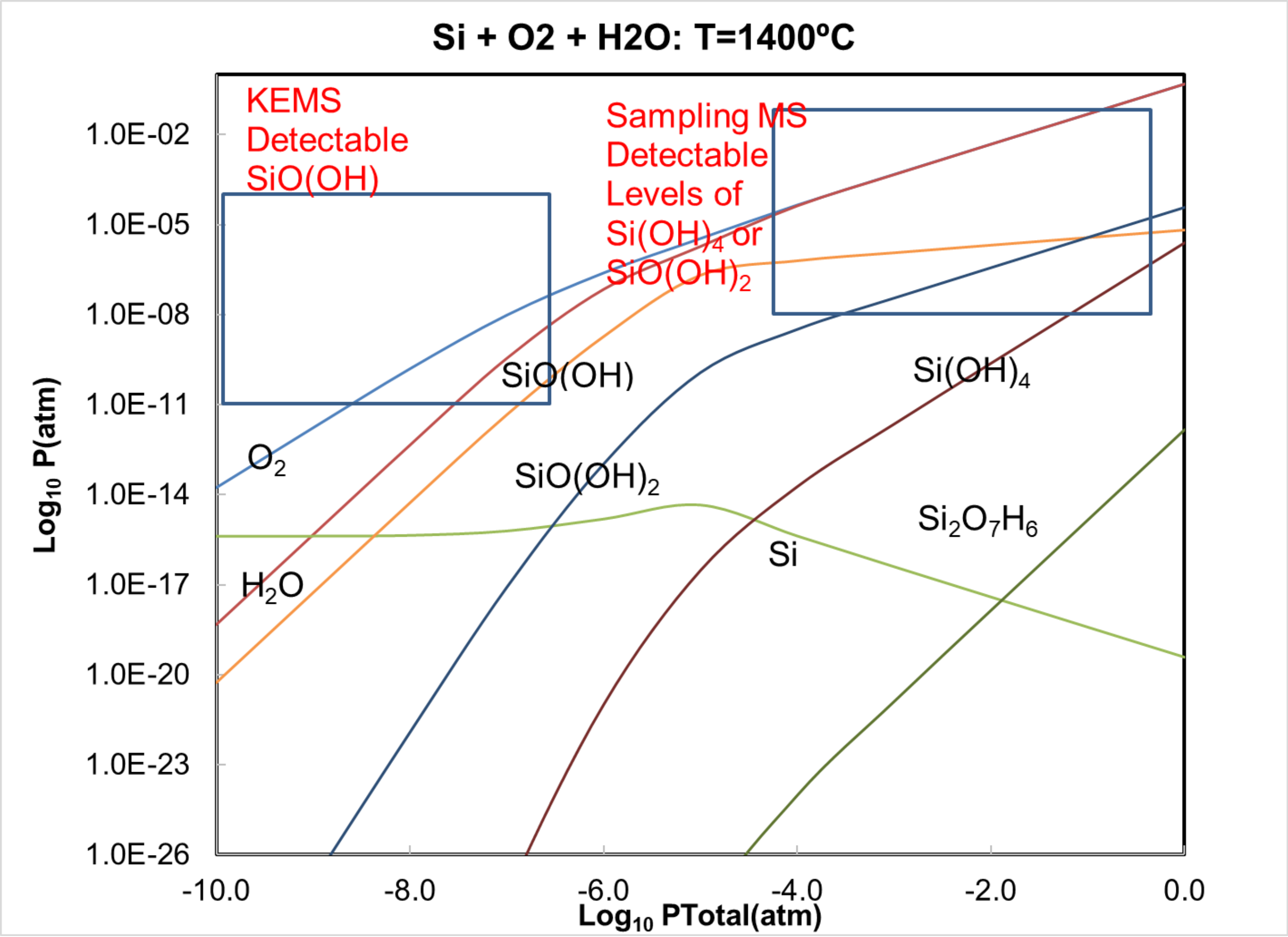
Knudsen Effusion Mass Spectrometer





- Resistance heated cell, Option of leaking small amount of gas into cell
- Measure partial pressures $P_i = \dfrac{kI_iT}{\sigma}$

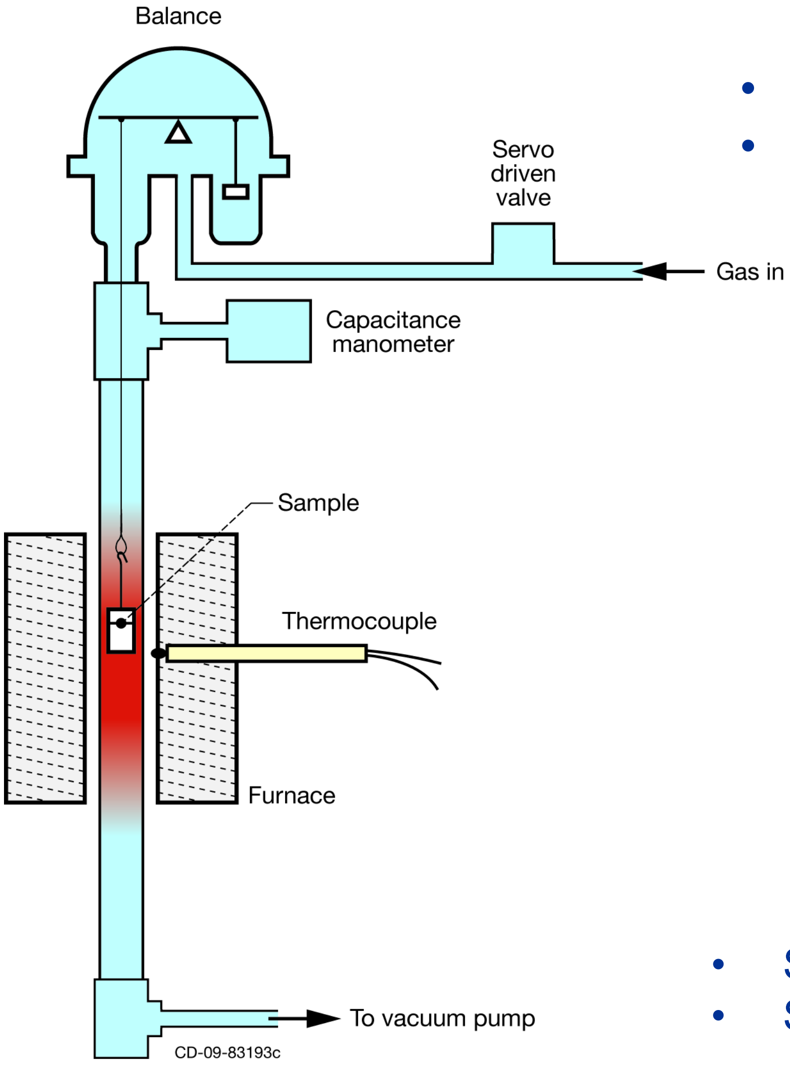
Different Vapor Species Important at Different Total Pressures: Need Different Experimental Methods



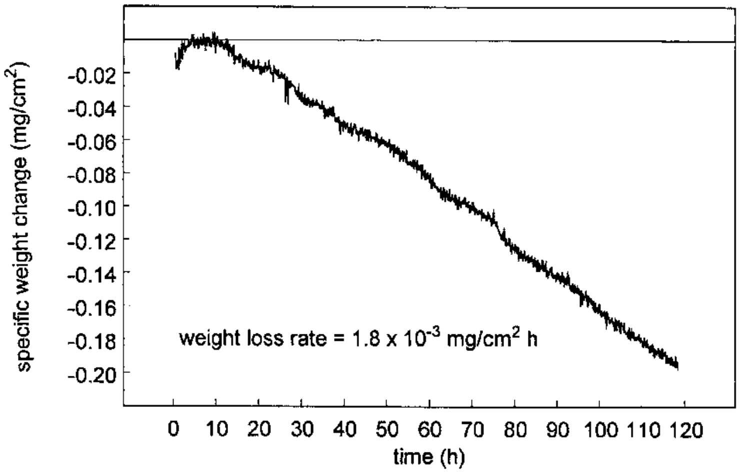
- Thermogravimetric system at higher total pressure
- Transpiration at ambient pressure
- Sampling mass spectrometry

Myers and Jacobson, Calphad, 2018.

Thermogravimetric Apparatus: NASA "Homemade"



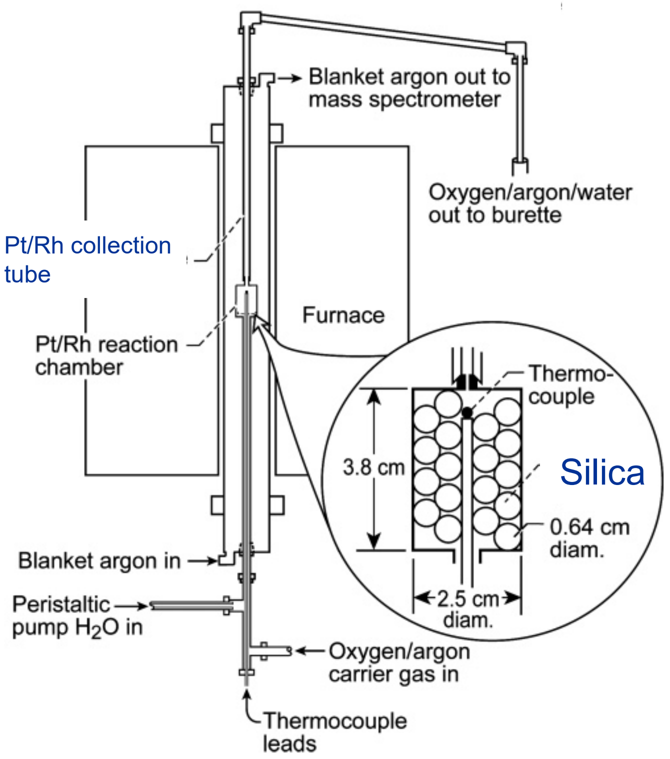
- Larger hot zone ⇒ larger samples
- Wide range of atmospheres possible
  - H_2O(g), CO_2(g), SO_2(g), Cl_2(g), 5%H_2/Ar



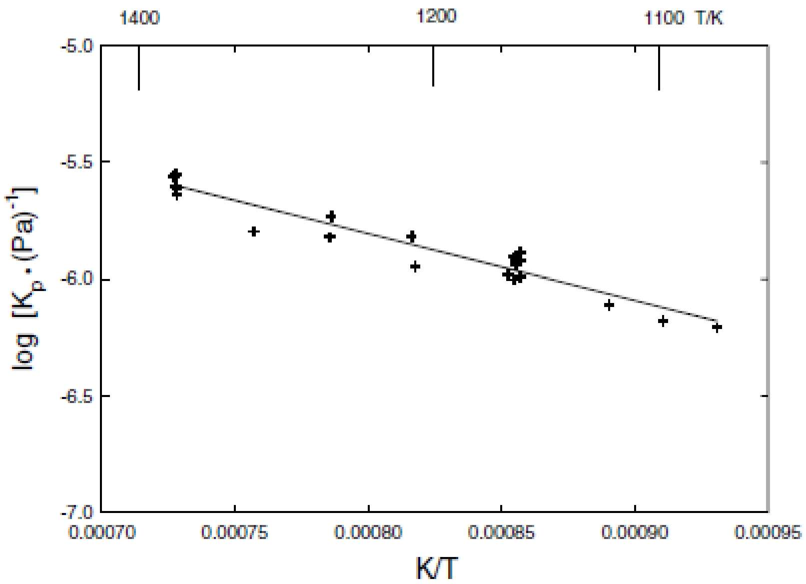
- Silica coupon in 50% H_2O/O_2 (Opila, JACerS, 1997)
- $SiO_2 + 2\ H_2O(g) = Si(OH)_4(g)$

Measure Vapor Pressures at high ambient pressures Transpiration Method

- Form vapor species, collect deposit downstream, analyze
- Adjust flow rates to assure equilibrium in reaction chamber
- Limited only by deposition rates and deposit analysis technique
  - SiO_2—easiest! Dissolve deposit in dilute HF and then use ICP-AES (μg)
  - Other oxides require more involved dissolution procedure (D. Johnson)
- Accurate technique for obtaining thermochemical data at 1 bar
- Used for Si-OH, Cr-OH, Ti-OH in our labs



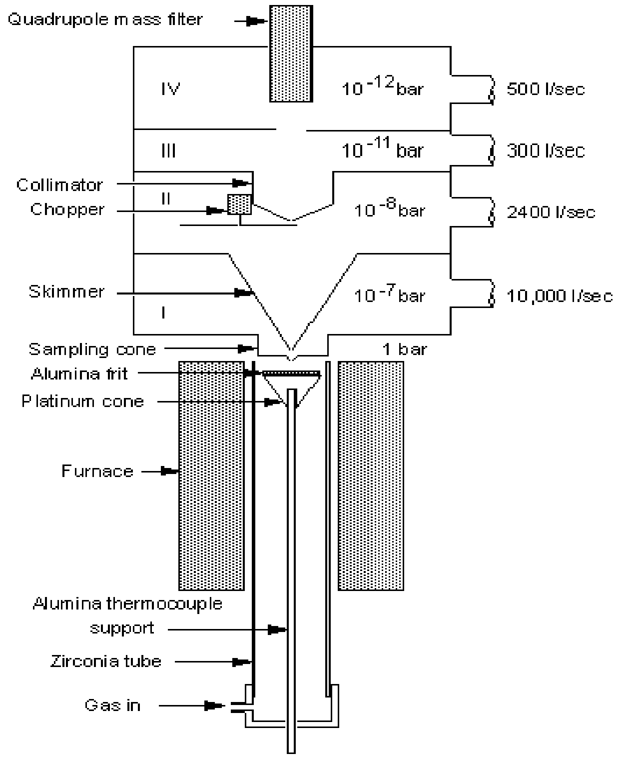
Results for $SiO_2 + H_2O$ Van't Hoff Plot: ln K vs 1/T



- $Si(OH)_4$ dominant species; Some evidence of $SiO(OH)_2$ at higher temperatures
- For $Si(OH)_4$: $\Delta_r H(1200\ K) = (54.6 \pm 2.7)$ kJ/mol; $\Delta_r S(1200\ K) = (67.5 \pm 2.1)$ J/mol-K
- Use computed or measured spectroscopic data to get heat capacities

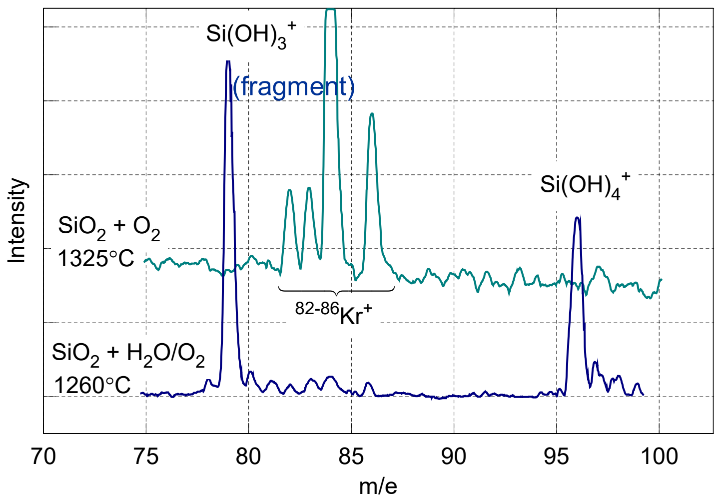
Jacobson et al. (2005), J. Chem. Therm. 37, 1130-7.

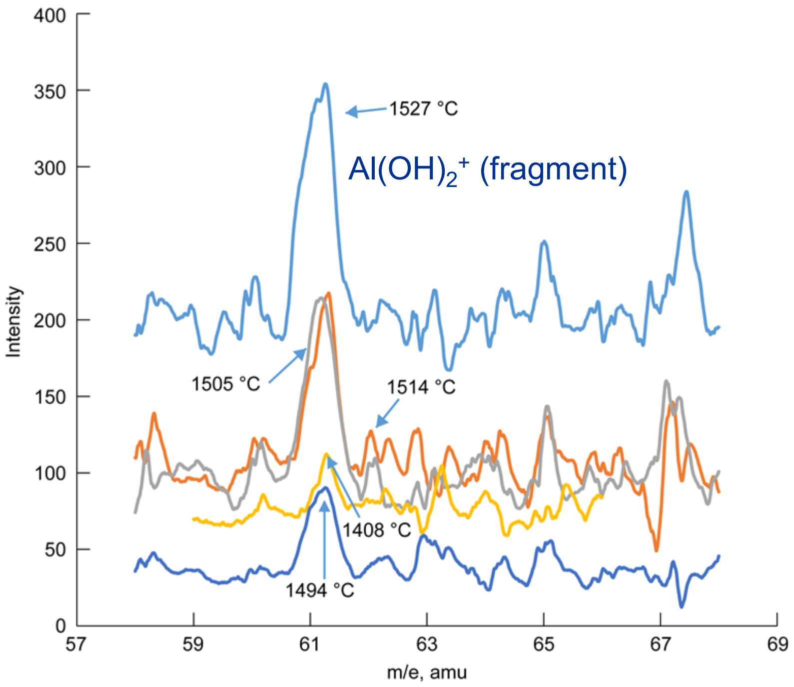
Sampling Mass Spectrometer



- Uses a free jet expansion to directly sample a one atmosphere process <u>without altering chemistry</u>
  - Gas/solid reaction which generate volatiles
  - Observe condensable species

First Direct Observations of $Si(OH)_4(g)$ and $Al(OH)_3(g)$





Opila et al., JACerS, 1997

Myers and Jacobson, Calphad, 2018.

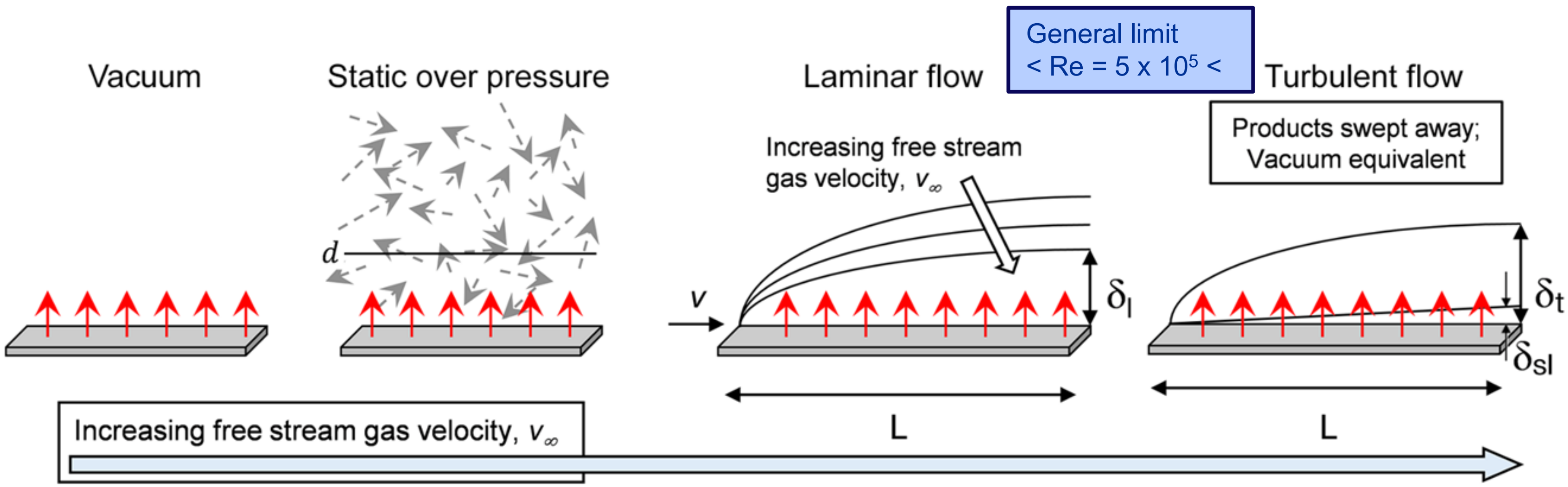
Thermodynamic data from Quantum Chemistry Methods (C. Bauschlicher/NASA Ames)

- In conjunction with experimental methods
- DFT and wave function methods
  - DFT—B3LYP gives basic molecular geometries, corrections then needed for internal rotations and anharmonicity
  - Higher level methods for enthalpies
- Input data: $\Delta_f H^o(298)$, $S^o(298)$, C_p
- Al-O-H, Si-O-H, Zr-O-H, Hf-O-H, Yb-OH, Gd-OH, Y-OH, Cr-O-H, Mn-O-H, La-O-H, Ta-O-H
- Database for computational thermodynamics codes/free energy minimizers: FactSage, ThermoCalc, SOLGASMIX, NASA CEA, etc.

Predicting Performance in Actual Environments

- Thermodynamic effects of overpressure:
  - $SiO_2(s) \rightarrow SiO_2(g)$ No effect
  - $SiO_2(s) \rightarrow SiO(g) + ½\ O_2(g)$ Small overpressure of O_2 will suppress vaporization significantly
- Thermodynamic Modeling
  - Free energy minimizer computer code
  - Input is solid oxide composition and over pressure (e.g. O_2, O, H_2O, etc.)
  - Minimizes free energy of all possible reactant products subject to constraint of mass conservation
  - Gives equilibrium vapor pressure for calculating mass loss
  - *Need accurate thermochemical data for all species*
- Kinetic
  - Static boundary layer which limits flow generally by orders of magnitude
- Surface changes

Vapor Pressures ⇒ Material Loss/Recession Rates



HKL equation

$$J_v = \frac{\alpha_v[P_{eq}(MO)]}{\sqrt{2\pi MRT}}$$

Fick's first law

$$J = -\frac{D}{RT}\frac{P_{surf}}{d}$$

Laminar flow

$$J_i = 0.665(Re)^{0.5}\,(Sc)^{0.33}\,\frac{D_i(\rho_{i,s})}{L}$$

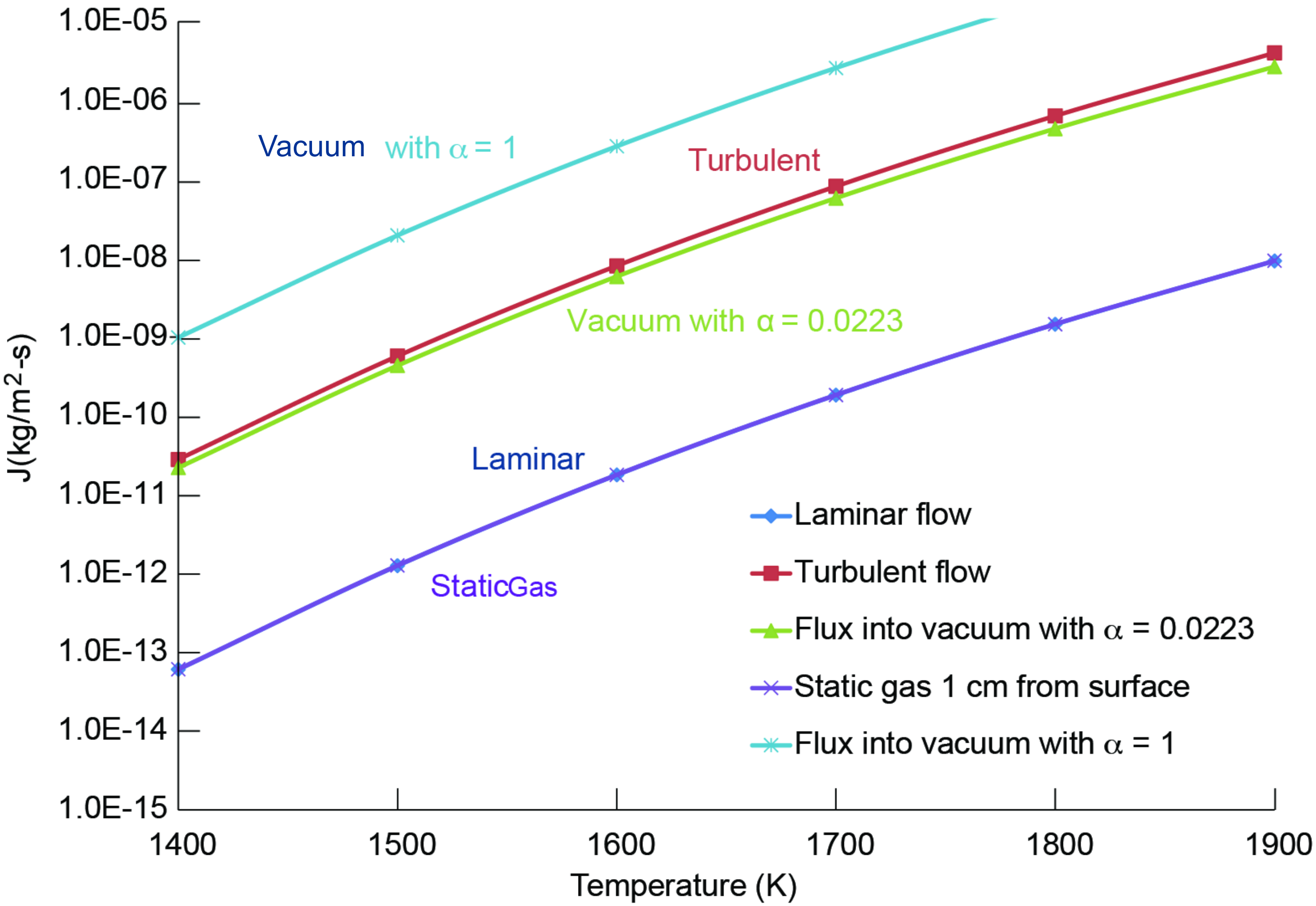
Turbulent flow

$$J_i = 0.0365\,(Re)^{0.8}(Sc)^{0.33}\,\frac{DiP_i}{RTL}$$

- Vapor pressure ⇒ flux (wt/(unit area-time)) or recession (length/(unit time))
- Inner viscous sublayer in turbulent flow becomes vanishingly thin

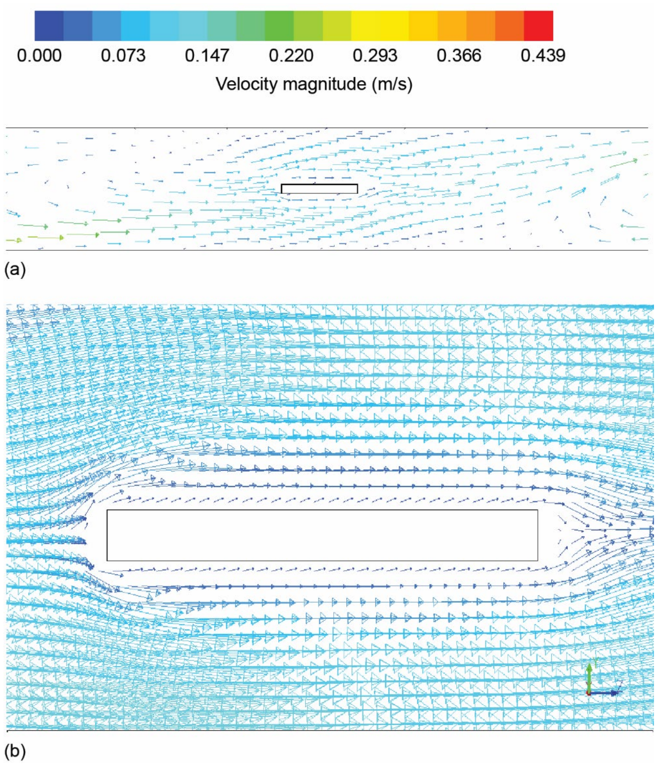
Jacobson, et al. (2020) Oxid. Met. 93, 247-82.

$SiO_2 \rightarrow SiO(g) + O_2(g)$ Vaporization into vacuum, static gas, laminar flow gas, and turbulent flow gas

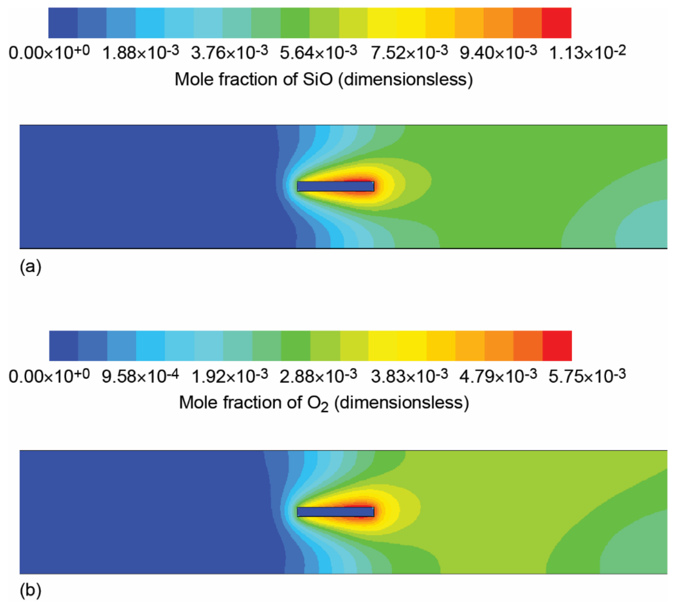


Laminar Flow Computational Fluid Dynamics (CFD) Results with Temperature Fixed Velocities and x(SiO), x(O_2) (M. Kuczmarski, GRC)

Velocity Vectors



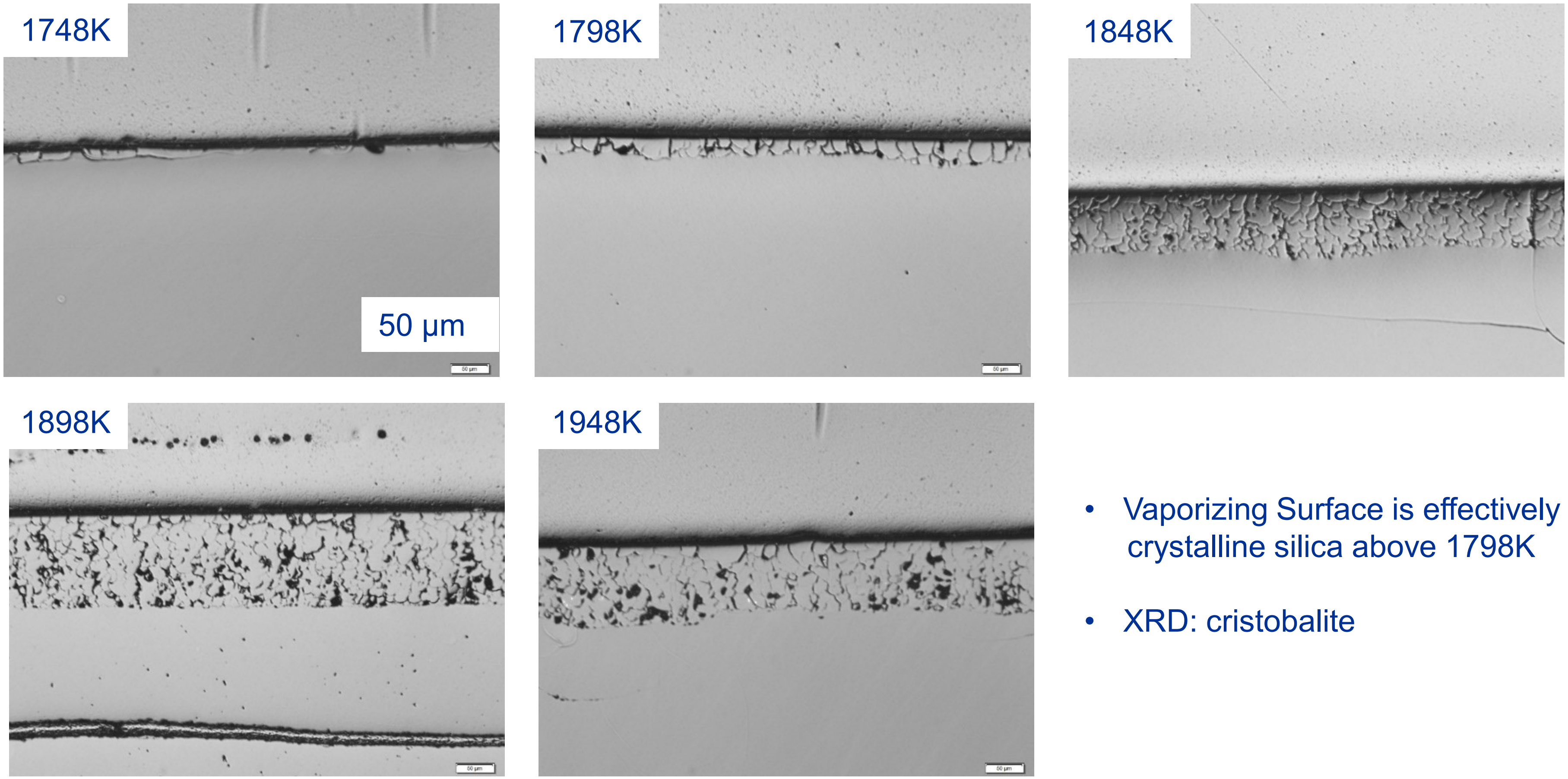
Concentration of Vapors



- Coupon disturbs flow: Boundary layer
- Distribution of SiO, O_2 after coupon

Jacobson, et al. (2020) Oxid. Met. 93, 247-82.

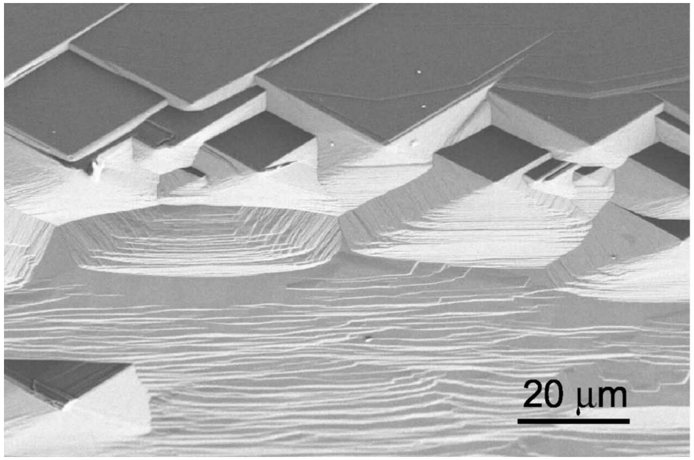
Crystallization of Fused Silica Outer Surface: 8 hrs at Temperature in vacuum



- Vaporizing Surface is effectively crystalline silica above 1798K
- XRD: cristobalite

Ingersoll et al., JECerS, 2017

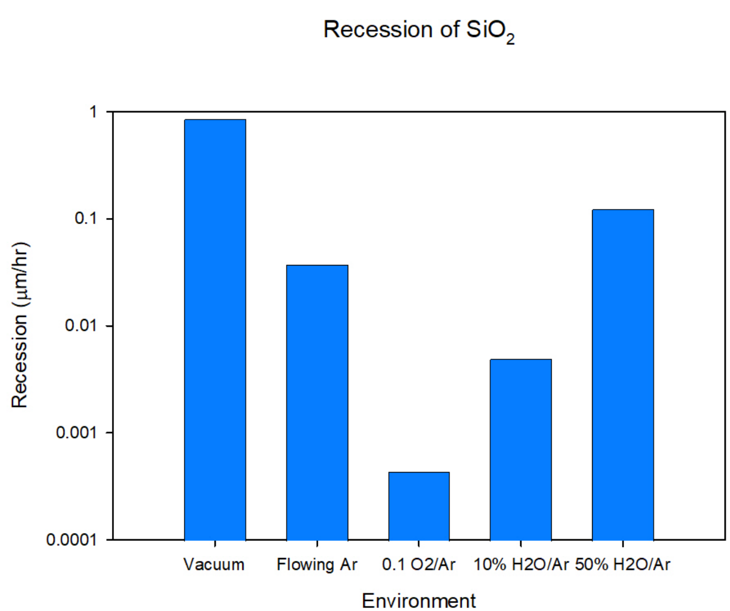
Al_2O_3 (sapphire) + H_2O Generates Etch Pits

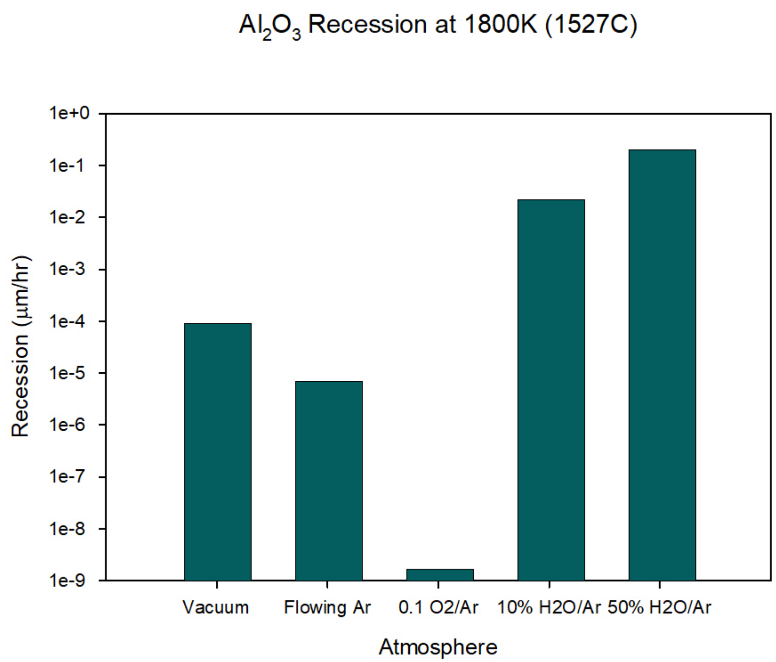


Micrographs of sapphire coupon edges after the following exposures: 1450°C, 68% H_2O, 72 h.

Opila and Myers, JACerS, 2004.

Performance in Different Environments: Recession at 1800K (1527C)





- Recession is suppressed by an overpressure of oxygen due to decomposition reaction
  - $SiO_2(s) \rightarrow SiO(g) + \frac{1}{2} O_2(g)$
  - $Al_2O_3(s) \rightarrow 2Al(g) + 3/2O_2(g)$
- Water vapor may enhance recession, depending on amount and energetics of reaction

Summary and Conclusions

- Silica and alumina (and other oxides) are very stable thermochemically
  - Still subject to chemical attack

- Routes of chemical attack
  - Dissolution (fluxing) from deposits
  - Vaporization in non-reactive gases
    - Vacuum
    - Flowing Ar
  - Vaporization in reactive gases
    - O_2 (suppresses vaporization in most, but not all cases)
    - H_2O (enhances vaporization)

- Experimental methods
  - Low ambient pressure: TGA and mass spectrometer
  - High ambient pressure: Transpiration, TGA, sampling mass spectrometer

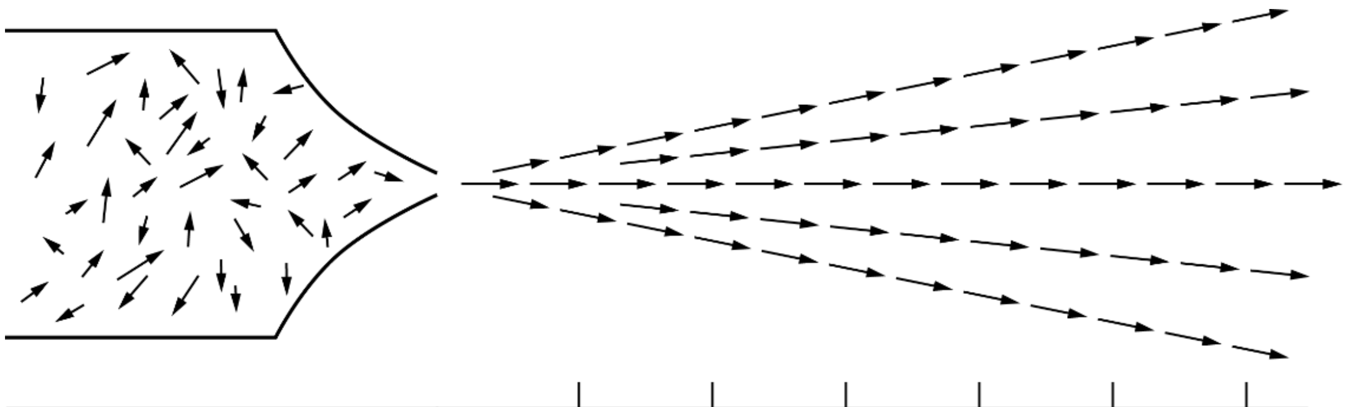
- Modeling/predicting attack
  - Need a good thermodynamic database and free energy minimizer code
  - Need fluid/environmental parameters
  - Surface changes

Supplemental Material

Free Jet Expansion

Atmosphere

Mass Spectrometer 10^{-8} torr
Preserves Chemical and
Dynamic Integrity of Process



Distance (X/D)	10	20	30	40	50	60
Mach number	15	24	32	38	44	50
Temperature (K)	4.0	1.6	0.9	0.6	0.5	0.4
Density (S. T. P. torr)	15	3.7	1.6	0.9	0.6	0.4
Pressure (mtorr)	150	15	3.5	1.5	0.7	0.4
Collisions (between 5 and X)	80	106	112	115	117	119

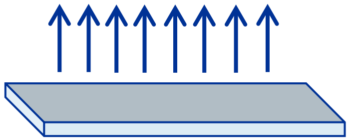
Miller,
Science
(1984)

- Use the mass spectrometer to directly sample vapors from a one atmosphere process
  - Gas/solid reaction—identify hydroxide species

Vaporization Coefficients

- Vapor Flux leaving a free surface into a vacuum

$$J(\max) = \frac{P_{eq}}{\sqrt{2\pi MRT}}$$

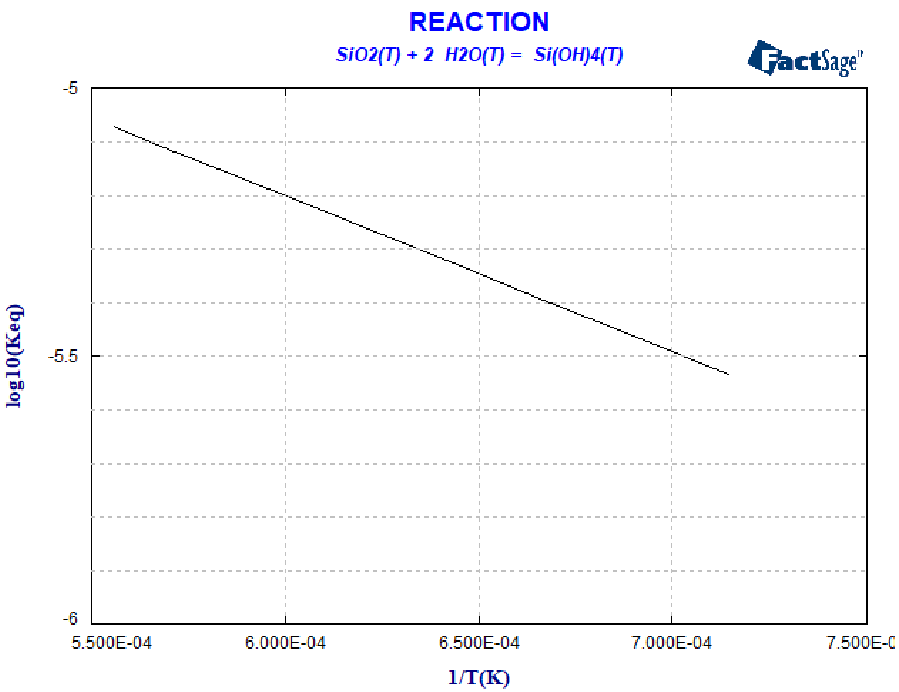


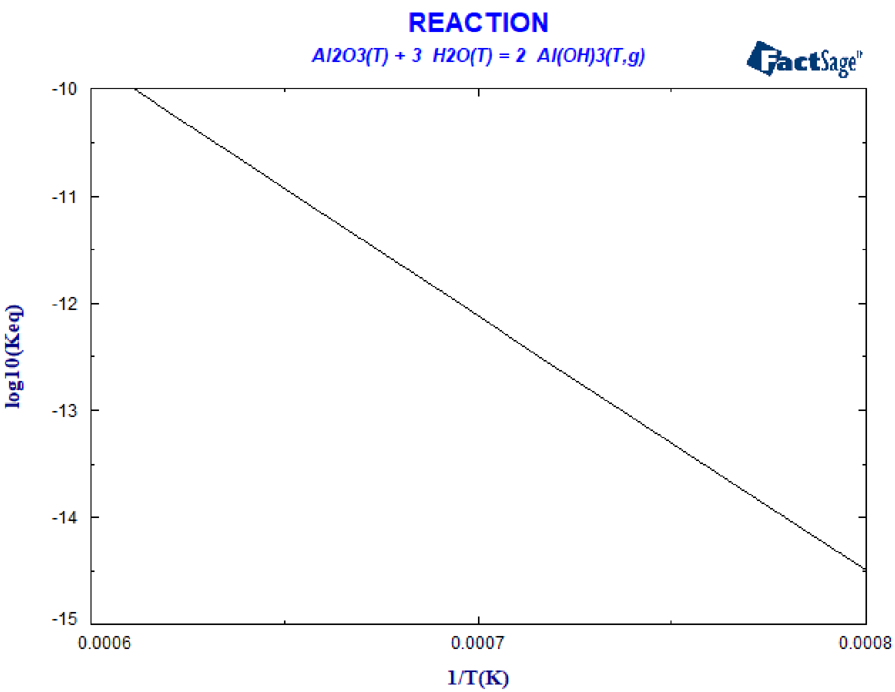
- Modified by a factor α: Vaporization Coefficient

$$J(\max) = \frac{\alpha P_{eq}}{\sqrt{2\pi MRT}}$$

  – Metals: Generally unity; Oxides 0.1 to 10^{-5}

- Condensation coefficient
  – Vapor flux striking a free surface—only a fraction of the equilibrium flux condenses on an oxide
  – Free surface vaporization = Langmuir vaporization


REACTION
SiO2(T) + 2 H2O(T) = Si(OH)4(T)
FactSage
-5
-5.5
-6
5.500E-04
6.000E-04
6.500E-04
7.000E-04
7.500E-0
1/T(K)
log10(Keq)


REACTION
Al2O3(T) + 3 H2O(T) = 2 Al(OH)3(T,g)
FactSage
-10
-11
-12
-13
-14
-15
0.0006
0.0007
0.0008
1/T(K)
log10(Keq)

MgO (001) Surface after Vaporization at 1873K